Research Article

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Development of a continuous PET depolymerization process as a basis for a back-to-monomer recycling method

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Abstract: This study presents a new approach for the recycling of bilayered PET waste in an efficient, continuous process with a depolymerization degree >97%. The complex PET waste was converted by chemolysis into its monomers ethylene glycol (EG) and the corresponding salt of terephthalic acid (TA) in a twin-screw extruder (TSE). Via this method, the starting materials for PET production were recovered, and highly contaminated PET waste and PET composite materials were transformed into valuable starting materials. The PE layer of the composite PET/PE material remained inert under depolymerization conditions and could be separated by filtration. An increase in the rotational speed by 200 rpm in the TSE reduced the residence time, but the degree of depolymerization was not affected in a proportional manner. Thus, the results indicate that a shorter residence time can be compensated with intensified mechanical agitation due to higher rotational speeds to obtain a similar degree of depolymerization. These results support the potential of this recycling concept to substantially contribute to the implementation of a circular PET economy.

Keywords: depolymerization, alkali hydrolysis, PET waste, chemical recycling, circular economy

Abbreviations

ATR	attenuated total reflection
BHET	bis(hydroxyethyl)terephthalate
BHETA	bis(2-hydroxy ethylene)terephthalamide
BMR	back-to-monomer recycling
b-PET	ground post-consumer PET bottles
D	screw diameter (mm)
DMT	dimethylterephthalate
δ	chemical shift (ppm)
ρ_{PE}	density of PE (g cm^{-3})
ρ_{PET}	density of PET (g cm^{-3})
EG	ethylene glycol
IR	infrared
L	screw length (mm)
m_0	mass of the initial PET waste (g)
$m_{residue}$	mass of unreacted solid (g)
DST	disodium terephthalate
NMR	nuclear magnetic resonance
PET	poly(ethylene terephthalate)
p-PET	colorless PE-coated PET material
rpm	revolutions per minute (min^{-1})
TA	terephthalic acid
T	temperature (°C)
t	time (s)
Δt	width of residence time distribution (s)
t_α	time of first color appeared (s)
t_{max}	time of maximum colored product (s)
t_ω	time when no color was detected anymore (s)
TSE	twin-screw extruder
x	depolymerization degree according to Eq. 3 (%)
y	depolymerization degree according to Eq. 4 (%)

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1 Introduction

Polymers allow for a wide range of properties that enable the modern economy to function more effectively. They are used in different areas, such as the automotive industry, electronics, and construction. However, due to their unique combination of high mechanical, chemical, and thermal stability combined with sensory inertness and light weight, packaging consumes the largest portion of worldwide polymer production [1]. Since packaging often has a very short first-use cycle, the plastic passes directly into the waste stream. In 2016, 260 million tons of plastic waste were produced worldwide [2]. These were 40% landfilled, representing unused resources [3]. Only 16% of the caused waste was collected for recycling, with the largest amount for mechanical recycling [3].

Poly(ethylene terephthalate) (PET) is a polymer that is often used for packaging. The present estimates suggest that PET production will increase to 73.4 million metric tons by 2020 [4]. A vast amount of the produced PET material is consumed by the packaging and textile industries for short-lived products. PET is resistant to many chemicals and is therefore well suited for packaging foods and liquids. Furthermore, some properties of PET can be specifically tailored during the production process. For example, the permeation propensity of O_2 and CO_2 can be reduced with increasing degrees of crystallinity. In addition to the mechanical requirements, packaging must also provide additional properties, such as a barrier to moisture or light. To meet these requirements in packaging, different polymers are often combined to ensure an economical product. So-called multilayer packaging consists of several layers of different polymers that are tailored to fulfill the manifold functions of packaging [5].

Thermomechanical recycling is a prevalent recycling technology and is only applicable for high-purity PET waste. Since the polymer chains are damaged in the process, this proportion of plastic waste also leaves the recycling loop after a few cycles. McKinsey & Company forecasts a volume of plastic waste of approximately 440 million tons by 2030 [3]. Most of the material must be produced from primary raw materials from fossil sources, as mechanical recycling does not achieve the required quality of the PET. In 2017, 0.92 million tons of PET were processed in Germany and were predominantly used for packaging. At the same time, 52.7% of these 6.15 million tons of plastic waste were used energetically and were thus lost in the recycling cycle as a resource.

Due to the lack of suitable technology, a large amount of PET waste in multilayer packaging and mixed plastics may not be properly sorted and is thereby sent to thermal recycling. Above the melting point, irreversible structural changes due to reactions, such as undesired hydrolysis, lead to deteriorated mechanical properties [6]. Current state-of-the-art technology is not capable of processing multilayered and opaque PET materials to form high-value products. These difficulties in recycling materials are addressed with the presented recycling technology.

1.1 Chemical recycling pathways

Pure and slightly colored PET waste can be recycled thermomechanically, but the recycling of multilayered and highly colored complex PET waste is still a major challenge in waste processing [7].

Back-to-monomer recycling (BMR) offers, in contrast to pyrolysis, an opportunity to overcome this issue by producing the corresponding monomers through depolymerization rather than the production of bulk petrochemicals [8].

BMR is possible via different reaction pathways displayed in Figure 1: hydrolysis, methanolysis, glycolysis, or aminolysis, and ammonolysis [9]. The hydrolysis of PET is either conducted in water using high temperatures, high pressure, and catalysts or by strong acids and bases [10–13]. Water acts as a weak nucleophile and breaks the ester bonds to form TA and EG [14]. Alternatively, strong bases, such as sodium hydroxide, can be used to attack the ester linkages to form the corresponding monosodium terephthalate salt and disodium terephthalate salt (DST) and EG [15]. The monomer TA is

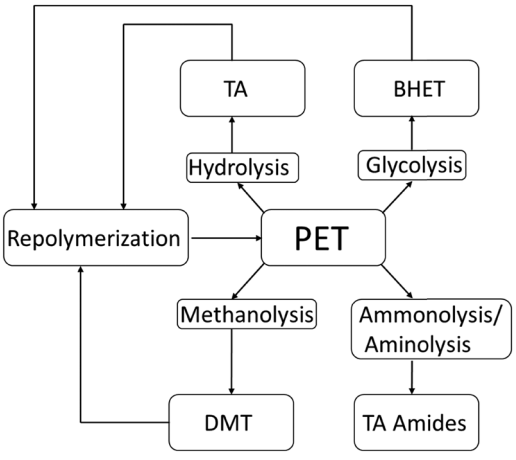

Figure 1: Different methods of PET chemical recycling paths, adapted from ref. [29].

recovered through the treatment of DST with a strong acid, such as hypochloric or sulfuric acid [7,15]. Several processes are based on alkaline hydrolysis. However, sodium hydroxide concentrations of up to 20 wt%, high temperatures of up to 250°C, and pressures between 1.4 and 2 MPa are mostly used for the depolymerization of PET [16,17].

During methanolysis, which has been thoroughly investigated by several groups, a transesterification reaction occurs, and dimethylterephthalate (DMT) and EG are produced [18–22]. This transesterification is usually catalyzed by sodium carbonate or zinc acetate [23,24]. This approach to PET recycling suffers from the formation of a mixture of several glycols, alcohols, and phthalic acid derivatives [22]. Downstream efforts to isolate and purify DMT diminish the economic viability of this process. However, methanolysis and glycolysis can be performed economically when pure PET waste is used as feed material, such as production waste [22]. During glycolysis, EG is used as a solvent and breaks the ester bonds of the polymer at high temperatures. This reaction is usually catalyzed by a transesterification catalyst, such as sodium carbonate, cobalt acetate, lead acetate, manganese acetate, and zinc acetate [20,25,26]. The reaction products include bis(hydroxyethyl)terephthalate (BHET), EG, and varying amounts of oligomers. This process benefits from the use of EG as a solvent, which is also produced during the process. The reaction rate of the depolymerization reaction has been found to be directly proportional to the polymer surface area [20]. This indicates that either a smaller polymer particle size or more vigorous mixing can lead to a more effective reaction. The most important disadvantages of methanolysis and glycolysis are the use of catalysts, high pressure and high temperatures during the process, and the resulting oligomers, which are difficult to separate from the products [22].

During aminolysis, PET is depolymerized with amine solutions, such as methylamine, allylamine, hydrazine, or ethanolamine [27]. During the process, bis(2-hydroxyethylene)terephthalamide (BHETA) is formed [27]. Alternatively, PET can be depolymerized by ammonolysis, where PET is treated with an aqueous ammonia solution to form terephthalamide [28].

A more detailed description of the advantages and disadvantages of the different approaches has been presented in several review articles [23,30].

In contrast to the known processes in the literature, the depolymerization is conducted in this study as a continuous process at ambient pressure, with short residence time, without catalyst, and at moderate temperatures.

1.2 Mechanism of PET depolymerization

Regarding the PET depolymerization mechanism, several research groups have investigated the reaction behavior of the solid/liquid interface between PET and the reaction solution. Yoshioka et al. investigated PET degradation in nitric and sulfuric acid and proposed a reaction mechanism for initial material degradation [31,32]. It is assumed that the reaction occurs on the surface of the material via a modified shrinking-core mechanism, where pores and cracks are formed during the reaction.

López-Fonseca et al. investigated the depolymerization mechanism of PET in aqueous media in the presence of a catalyst. They observed a lamellar reaction behavior on the external surface of the PET particles [33]. By contrast, Oku et al. reported that the reaction of PET with sodium hydroxide in EG appears to be a two-stage process with a fast initial reaction step and a slow second stage. They proposed that reaction products, such as DST, are formed on the surface of the PET particle and limit the rate of reaction [15].

Even though different reagents were used in the aforementioned studies, the results suggest that mechanical stress and constant renewal of the PET particle surfaces lead to a higher reaction rate.

1.3 Chemical depolymerization as a continuous process

While laboratory investigations on reaction pathways and kinetics are typically conducted in batch experiments, a transfer to an industrial application will benefit from a continuous operation. Given the enormous quantities of the PET recycling market, developing a continuous process seems mandatory from both an economic and ecological perspective. Initial studies have shown that the chemical recycling of PET has to overcome economic issues. In their study, Aguado et al. demonstrated that, from an economic perspective, wastewater management has a large impact on the feasibility of the recycling process in the alkaline hydrolysis of PET waste [7].

The processes described earlier show a reaction time ranging between 6 min and 70 h, typically achieved in batch processes [16]. Continuous production processes offer many advantages, especially with respect to constant product quality, automated operability and control, energy, and resource efficiency, as well as scalability. As shown for polymerization, batch processes have several disadvantages, such as high operating costs due to

product changeover, including intensive cleaning procedures and the risk of poor batch-to-batch consistency. Furthermore, batch processes are difficult to scale up due to the limited capability of heat transfer, which requires low reaction rates and results in longer batch times [34].

In the past, few attempts have been made to implement a continuous process with short reaction times for the recycling PET scrap material. Ostrowski described the continuous depolymerization of polyester at atmospheric pressure in EG at 230°C. The reaction was performed in a fed-batch reactor and was operated continuously [35]. The residence time was 1.5–3.6 h, and the resulting product was a mixture of various oligomers. Bergmann et al. reported a method to glycolyze PET waste with EG in a twin-screw extruder to produce oligomers with short chain length. The average residence time of the reaction mixture varied between 1 and 5 min. However, these investigations focused on online monitoring of the reaction rather than the recycling of the PET material [36].

The first experimental realization of continuous depolymerization of PET scrap material with sodium hydroxide to form EG and disodium terephthalate was described by Benzaria et al. in the patent US5545746 [37]. The reaction was performed in a kneading extruder with an approximately 6 min residence time at 120–160°C. They observed a depolymerization degree above 60% and could recover the EG formed directly during the depolymerization. Even greater depolymerization degrees >95% were achieved when a second downstream process step was introduced, where the raw product was tempered at 80–130°C for 30 min [37]. This approach presents a distinct improvement over the typically conducted batch reactions because of the rather short reaction times, the low temperatures, and solvent-free conditions [37]. The authors hypothesized that the mechanical stress in the kneading extruder accelerated the depolymerization reaction. The investigated process concept presented here follows a similar approach to the depolymerizing PET with a strong base to produce TA and EG. The authors developed a novel concept for process intensification for PET depolymerization. A twin-screw extruder was used to achieve more rigorous mechanical stress. This led to a high degree of depolymerization, with a residence time below 1 min. The "hydrolysis" route, as displayed in Figure 1, benefits from the fact that the resulting TA can be used without further processing for the production of PET in contrast to DMT and therefore functions as a "drop-in" building block for the current PET production [38].

The global increase in plastic production and the consequently generated PET waste have led to the need for new approaches for plastic waste recycling since the state-of-the-art technology is not capable of closing the material loop. In the past few decades, many studies have described the depolymerization of PET and the regain of the monomers TA and EG. In this study, the development of a continuous process to solve the issues associated with the various approaches for the chemical recycling of PET is proposed.

2 Materials and methods

2.1 Process concept and experimental setup for the continuous depolymerization of PET

2.1.1 Process concept

In this approach, the alkaline hydrolysis of polyesters is investigated as a method to recover TA and EG from PET scrap material in a continuous process. The depolymerization of PET is conducted in a three-phase system of solid PET, the solvent EG, which is produced during depolymerization, and the corresponding base solid sodium hydroxide. The underlying chemical reaction is displayed in Figure 2.

For compounding applications where mechanical stress and mixing are key requirements, twin-screw extruders are

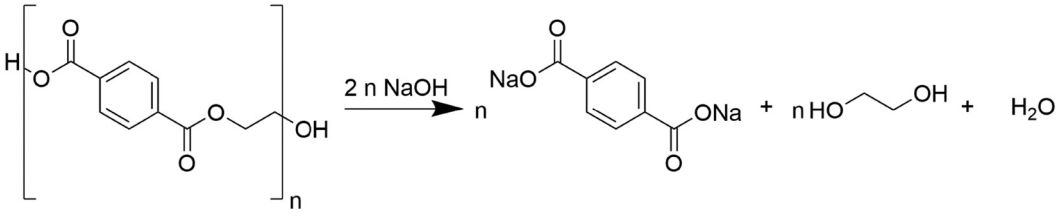

Figure 2: Reaction scheme of the PET depolymerization.

frequently used [39]. Therefore, such a device was selected to ensure high mechanical stress on the starting materials, as well as distinct mixing.

2.1.2 Experimental setup

The depolymerization experiments were conducted on a Leistritz, Nuremberg, ZSE 27 MAXX twin-screw extruder with a k-tron doser supplied by Coperion GmbH, Stuttgart. The screws had a diameter of 28.3 mm and an L/D ratio of 60. The twin screws consisted of 82 segments, which could be selected as mixing, holding, or kneading elements to create high shear stress and residence times. The screw design provided several reaction zones where the reaction mixture was intensely blended and put under mechanical stress with kneading elements. The PET material was dispensed in the main shaft using a gravimetric doser by k-tron (K-CL-SFS-KQX4), as displayed in Figure 3. Solid sodium hydroxide was fed through a side feed LSB27 in cylinder 4 and dispensed with a gravimetric doser (K-SFS-I 240 N). The chemicals as well as the extruder screw were flushed with N_2. Water was dispensed in cylinder 12 with a gravimetric pump (K-CL-SFS-P).

2.2 Reagents and PET samples

2.2.1 Light blue PET flakes (b-PET)

Light blue, washed, and dried ground postconsumer PET bottles were supplied by LINPAC Packaging GmbH, Ritterhude. The material was ground by Fraunhofer-Institut für Chemische Technologie (ICT), Pfinztal, to yield flakes (<3 mm in length × <3 mm in diameter) and used as the standard substrate without further processing.

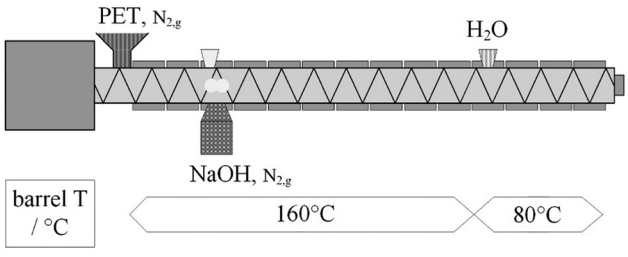

Figure 3: Configuration of the reactive extrusion process.

2.2.2 PE/PET flakes (p-PET)

The food packaging industry often uses composite materials consisting of PET and other polymers, such as polypropylene, polyethylene, or ethylene vinyl alcohol, to improve the properties of the packaging, such as oxygen permeability [5]. These multilayered packaging materials are difficult to recycle with thermomechanical methods, and it is unclear whether a PE-laminated PET material can be depolymerized with chemical methods as effectively and efficiently as a pure PET material. Therefore, production waste consisting of colorless, dry, and PE-coated PET material (PE/PET) was used as a model substrate. The material was supplied by W.u.H. Fernholz GmbH & Co. KG, Meinerzhagen. It was ground with a RETSCH, Haan, SM 300 cutting mill to flakes (<3 mm in length × <3 mm in diameter) and used without further processing. The PE coating thickness was stated as 27 µm by the producer, and the overall thickness was measured using a micrometer screw gauge and was 623 µm. The PET content was calculated via Eq. 1 with the density of PET $\rho_{PET} = 1.38\ g\ cm^{-3}$ and the density of PE $\rho_{PE} = 0.93\ g\ cm^{-3}$ [40,41].

$$\begin{aligned}\omega_{PET} &= \frac{m_{PET}}{m_{tot}} \\ &= \frac{V_{PET}\cdot\rho_{PET}}{V_{PET}\cdot\rho_{PET} + V_{PE}\cdot\rho_{PE}} \\ &= \frac{(\bar{\delta}_{tot} - \delta_{PE})\cdot\rho_{PET}}{\delta_{PE}\cdot\rho_{PE} + (\bar{\delta}_{tot} - \delta_{PE})\cdot\rho_{PET}} \\ &= \frac{(623\ \mu m - 27\ \mu m)\cdot 1.38\ g\ cm^{-3}}{27\ \mu m\cdot 0.93\ g\ cm^{-3} + (623\ \mu m - 27\ \mu m)\cdot 1.38\ g\ cm^{-3}} \\ &= 0.97\ \triangleq\ 97\%\ (w/w)\end{aligned} \quad (1)$$

2.2.3 Reagents

Commercially available sodium hydroxide (purity ≥98%, solid pearls with diameter <3 mm), sulfuric acid (25%, p.a.), and dimethylformamide (purity ≥99.5%) were used without further purification and were supplied by Carl Roth GmbH + Co. KG, Karlsruhe. The color masterbatch HT VPE 12220 was supplied by Treffert GmbH, Bingen.

2.3 Experimental procedure and parameters

2.3.1 Depolymerization experiments

The depolymerization experiments were started after the extruder was heated up to operating conditions. During

the experiments with the ZSE 27, the temperature was kept constant at 160°C for all experiments in all barrels except for barrels 1 and 11–15. There, the water was dispersed at 80°C, as displayed in Figure 3. The throughputs of the dosing units were gradually increased until the desired values were reached. The PET/NaOH/water ratio was held constant for all experiments at 1:0.44:1.43 $kg^{-1}\,kg^{-1}\,kg^{-1}$ at a constant total feed rate of 20 $kg\,h^{-1}$. As soon as the stationary state was reached, samples for the subsequent analysis were taken, and residence time measurement was started. The depolymerization of b-PET at a rotating speed of 200 min^{-1} served as a reference point for the evaluation of the results. The temperature of the barrels and the ratio of the mass flows were kept constant. The varied parameters of the experiments are displayed in Table 1. The average residence time of the product was adjusted by the rotating speed, which varied between 200 and 400 min^{-1}.

The resulting reaction product disodium terephthalate was dissolved in the water injected in cylinder 12, and a saturated suspension of disodium terephthalate, EG, PET, and NaOH exited the extruder. The resulting product was a white paste that could be collected and analyzed, as described in Section 3.3.

2.3.2 Residence time measurement

The residence time of the reaction mixture in the twin-screw extruder was measured by adding 100 mg of the masterbatch VPE 12220 to the main shaft and visual observation of the color change of the extrudate. Because the extrudate is opaque and strongly basic, the residence time was determined by qualitative visual assessment of the color intensity, following the investigations by Yalçinyuva et al. and Patterson [42,43]. Three points of the residence time have been determined: t_α the time until the first colored product appeared, t_{max} the time of the maximum color peak and most intensely-colored product, and t_ω the time when color was no longer detected. The measurements were conducted as a triplicate. The normalized width of the residence time distribution was introduced to assess the influence of the feed material and the rotational speed on the residence time characteristics (see Eq. 2).

$$\frac{\Delta t}{t_{max}} = \frac{t_\omega - t_\alpha}{t_{max}} \tag{2}$$

2.4 Data extraction and analytics

2.4.1 Degree of depolymerization

The degree of depolymerization can be calculated according to Eq. 3, as proposed by Hu et al. and Siddiqui et al. [44,45].

$$x(\%) = \frac{m_0 - m_{residue}}{m_0} \cdot 100 \tag{3}$$

where m_0 is the mass of the initial PET waste, $m_{residue}$ is the mass of unreacted solid, and x is the depolymerization degree. This is a viable approach for the determination of the degree of depolymerization of PET in batch reactions. In this study, a continuous process for the depolymerization of PET waste through alkaline ester hydrolysis was developed. Due to back mixing by some screw elements, there was no ideal plug flow in the extruder. Therefore, the mass of the initial PET m_0 from Eq. 3, which has entered the sample, cannot be determined exactly at moderate sampling rates in the order of minutes [39,46].

To determine the degree of depolymerization, an extrudate sample (approx. 20 g) was dissolved in deionized water and filtered. The residue was collected and dried to constant weight. The filtrate was treated with an excess amount of sulfuric acid to precipitate TA quantitatively. The precipitate was filtered off the solution, washed, and dried for at least 48 h at 80°C until constant weight.

Table 1: Experimental conditions and results

Experiment no.	PET nature	Speed (rpm)	y degree of depolymerization (%)	Absorbance of regained TA at 340 nm	t_{max} (s)	t_α (s)	t_ω (s)	$\Delta t/t_{max}$
1	b-PET	200	97.3	1.089	58	47	95	0.83
2	b-PET	300	98.3	1.170	43	34	75	0.95
3	b-PET	400	97.7	1.195	36	27	67	1.11
4	p-PET	200	97[a]	0.744	53	43	90	0.89
5	p-PET	400	97[a]	0.793	32	23	73	1.56

[a] The results for p-PET are a minimum estimate considering the content of PE.

The degree of PET depolymerization was then determined by Eq. 4:

$$y(\%) = \frac{n_{TA}}{n_{TA} + n_{residue}} \cdot 100 \quad (4)$$

where n_{TA} is the amount of terephthalic acid in the sample in mol and $n_{residue}$ is the amount of unreacted polymer in the sample in mol according to the molecular weight of the repeat unit of PET.

Eq. 3 is valid only for pure PET samples and can be used as a minimum estimate for contaminated PET waste or coated PET material as p-PET with a high PET content. Extensive studies on balancing have shown that Eq. 4 leads to values with the smallest variations. Eq. 4 focuses on the yield in TA and assumes the formation of EG in stoichiometric amounts according to the reaction scheme in Figure 2.

2.4.2 Infrared spectroscopy

Infrared (IR) spectra were recorded by attenuated total reflection (ATR) with a Bruker Tensor 27 FT-IR spectrometer. Commercial terephthalic acid (ACROS Organics, Fair Lawn) was used for calibration to compare with the generated products.

2.4.3 NMR spectroscopy

All spectra were recorded on Bruker AVIII-400 or AV600, and chemical shift δ values are stated in ppm relative to Me_4Si, as internal standard and coupling constants J are stated in Hz. The spectra were obtained in d_6-DMSO solution.

2.4.4 UV/Vis-spectrometry

The color index of the TA is a technically relevant parameter for the quality of the TA. A sample of terephthalic acid (0.5 g, 0.003 mol) was dissolved in 10 mL dimethylformamide. The TA solution was transferred into a quartz cuvette with a path length of 1 cm, and the absorbance was measured from 230 to 900 nm with a Jena Analytik AG, Jena, Specord 210 Plus spectrometer.

3 Results and discussion

The following section presents and discusses the experimental results for the depolymerization of PET waste. This study intends to provide a proof of concept of the approach by processing two different model substrates in an extruder to produce TA.

3.1 Depolymerization of PET (light blue)

With the setup displayed in Figure 3, the influence of rotational speed on the degree of depolymerization was investigated. The rotational speed varied from 200 to 400 min^{-1}. At each operating point, the residence time was measured, and a sample was taken to determine the degree of depolymerization. As depicted in Figure 4, a depolymerization degree above 97% was achieved in all experiments, with the highest degree of depolymerization observed at a rotational speed of 300 min^{-1}. At a rotational speed less than 200 min^{-1}, the feed rate exceeded the extruders' conveying capability and thus the torque limit of the device.

The characteristic residence times in the extruder are displayed in Figure 5 and Table 1. All residence times were reduced with the increasing rotational speed. Moreover, the plot shows that the residence time distribution broadens with a reduced rotational speed. These results are in line with the assumption of plug flow in an extruder, as suggested by Shon et al. [47]. The rotational speed of 200 min^{-1} is taken as a reference, with a degree of depolymerization of 97.3% at a residence time at color maximum of $t_{max} \approx 58$ s.

According to Oku et al., the PET depolymerization reaction is a two-stage process in which the lower rate constant represents the coverage of the surface with disodium terephthalate [15]. The results presented here

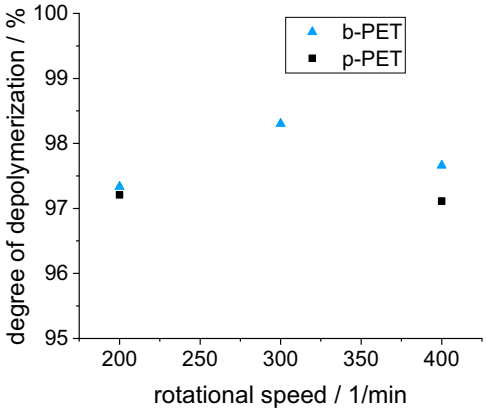

Figure 4: Influence of rotational speed on the degree of depolymerization of b-PET and p-PET calculated according to Eq. 4.

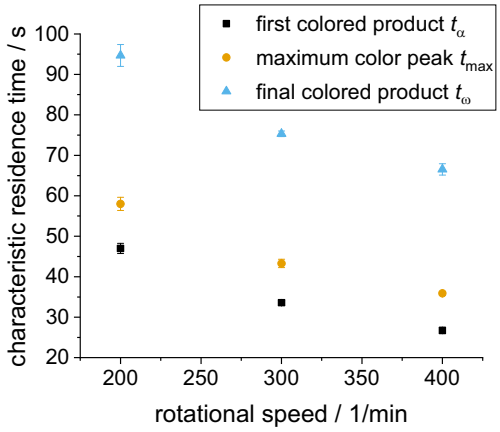

Figure 5: Influence of rotational speed on characteristic residence times of the extrudate for b-PET.

suggest that better mixing and higher shear stress on the material can compensate for a lower residence time in the twin-screw extruder.

In consideration of the results displayed in Figure 5, residence time cannot be the only factor influencing the degree of depolymerization. The residence time t_{max} was reduced by 38% when the rotational speed was doubled from 200 to 400 min^{-1}, but the degree of depolymerization was reduced by only 0.3%. High shear stress and mechanical work on the polymer from the extruder screws led to higher depolymerization of the PET material at higher rotational speeds through faster renewal of the PET reaction surface. In addition, the intense mixing of the extruder led to a constant renewal of the reaction mixture in the proximity of the surface of the PET particles, resulting in a very high PET turnover at a residence time of 36 s at 400 min^{-1}.

3.2 Depolymerization of PE/PET material

In addition to light blue PET flakes, a PET composite material consisting of PET and PE was used as a feed material for the depolymerization process. The results, displayed in Figure 4, clearly show that the depolymerization of PET is not affected in great measure and that high yields of TA are obtained even though the PET material is covered on one side with a quasi-inert layer and the residence time in the extruder is very short. This might be due to a delamination process of the p-PET flakes through mixing and high shear stress in the extruder.

According to Table 1, the residence time t_{max} of the p-PET material is 6 s lower at a rotational speed of 200 min^{-1} and 4 s lower at a rotational speed of 400 min^{-1}, which might be due to the content of the inert PE material in p-PET (see Figure 6).

3.3 Comparison of the residence times of b-PET and p-PET

To compare the residence times of the two PET materials, the width of the residence time was calculated by the time of maximum coloration (see Eq. 2). These residence time coefficients are shown in Figure 7. For all experiments, the normalized residence time for p-PET was larger than for b-PET. At a rotational speed of 400 min^{-1}, the coefficient of the p-PET was 28% higher than the coefficient of the b-PET. During the depolymerization of the p-PET material, the PE flakes were maintained, resulting in a broader residence time distribution.

3.4 Characterization of depolymerization products

The extruder output was treated as described in Section 2.4.1 to receive TA and unreacted PE and PET residues. Figure 8 displays the absorbance of the TA samples from 330 to 350 nm. It is clearly recognizable that the postproduction waste material p-PET results in lower absorption values, indicating a higher TA quality. The absorbance values of TA from b-PET are higher, presumably due to the content of blue particles and the fact that b-PET is a postconsumer material.

Furthermore, a higher rotary speed resulted in a higher absorbance, which indicated the formation of undesired colored contaminants at high rotary speeds.

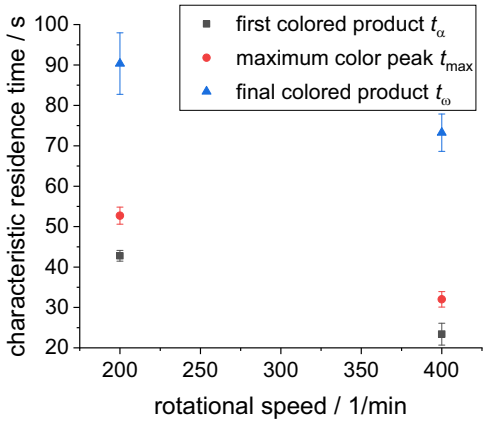

Figure 6: Influence of rotational speed on the characteristic residence times of the extrudate for p-PET.

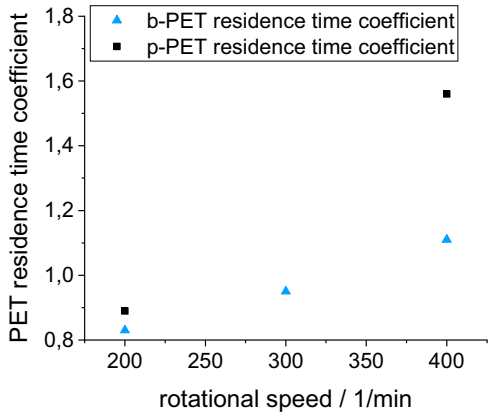

Figure 7: Residence time coefficients of b-PET and p-PET.

As a representative example, Figure 9 and Table 2 present the results of the NMR analysis of p-PET at a rotary speed 200 min^{-1}. The ^{1}H-NMR-spectra in Figure 9 show that a mixture of the isomers TA and IPA has been isolated. No EG residues or CH_2 groups are present within the detection limit of approximately 1% of the NMR spectra. The depolymerization of PET to TA/IPA and EG seems to be complete since no oligomers, such as corresponding CH_2-groups, have been observed. Since recycled bottle flakes have been used as a feed material, an IPA content of 1–5 (w/w)% was expected. Usually, IPA is added during the production of PET to influence its crystallinity and mechanical properties [48].

3.5 Comparison of recycled TA vs standard commercial TA

All TA samples were characterized by IR spectroscopy, and the obtained spectra were compared with the commercially available TA standard (see Figure 10). Obviously, the IR spectrum of the recovered TA matches very closely with the corresponding spectrum of the commercial standard. At 3000–2900 cm^{-1}, the C–H phenyl stretching band was observed, and at 1668 cm^{-1}, the intense C=O-group stretching band indicated the presence of a carbonyl group. At 1422 and 878 cm^{-1}, OH-group bands were visible, as described by Téllez et al. [49]. The absorption peak at 783 cm^{-1} proves the paraposition of the carboxyl groups in the obtained terephthalic acid [45].

Therefore, it was concluded that the obtained product was mainly monomer terephthalic acid with a small amount of isophthalic acid. In further experiments, the suitability of terephthalic acid for polymerization with EG to PET will be tested.

3.6 Characterization of the depolymerization residue

The residues of Experiments 1 and 2 were analyzed by IR spectroscopy, and four intense bands were detected (see Figure 11). Between 3000 and 2800 cm^{-1}, the absorption bands of the CH_2-groups were observed at 1470 cm^{-1}, and the deformation band of CH_2-groups and the CH_2 rocking band were observed at 715 cm^{-1}. These four characteristic intense bands show that the residue mainly consists of PE [50,51]. In comparison, the FTIR-spectrum of the starting material p-PET shows characteristic peaks for PET, such as the C–H phenyl stretching band at 3000 and 2900 cm^{-1} and the carbonyl-group band at 1713 cm^{-1}. Polyolefinic constituents of PET-containing waste appear inert under the given PET depolymerization

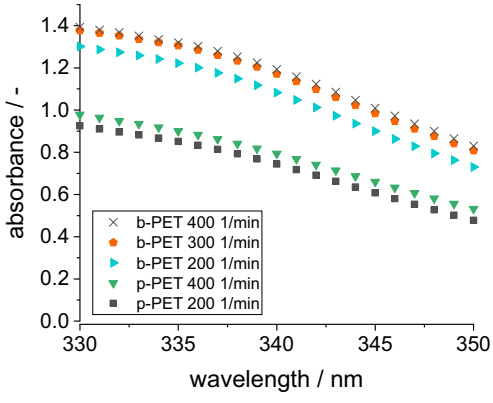

Figure 8: UV/Vis-spectra of the obtained TA in DMF (50 g/L) solution at a wavelength of 330–350 nm.

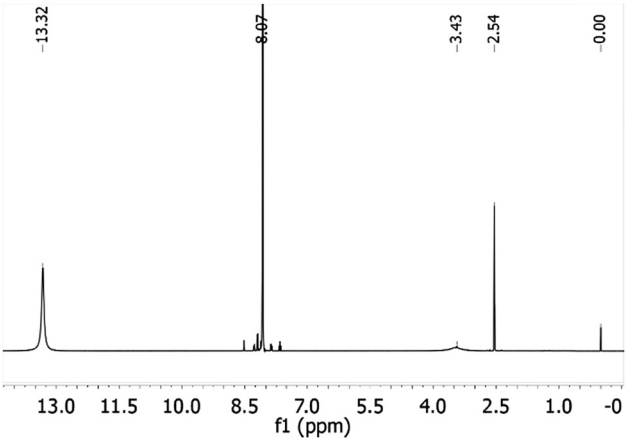

Figure 9: ^{1}H-NMR-Spectra of the obtained TA/IPA mixture from p-PET material.

Table 2: Results of the ^{1}H- and ^{13}C-NMR-analysis of Experiments 1 and 4 (cf. Table 1)

Experiment no.	Process conditions	Compound	Corresponding NMR signals
1	b-PET, 200 min^{-1}	Terephthalic acid	**^{1}H-NMR** (d_6-DMSO, 400 MHz): δ = 8.06 (s, 4H), 13.31 (s, 2H) ppm
			^{13}C-NMR (d_6-DMSO, 100 MHz): δ = 129.49 (d), 134.49 (s), 166.71 (s) ppm
		Isophthalic acid	**^{1}H-NMR** (d_6-DMSO, 400 MHz): δ = 7.67 (t, J = 7.64 Hz, 1H), 8.19 (dd, J = 1.76, 7.72 Hz, 1H),.. 8.52 (t, J = 1.76 Hz, 1H), 13.31 (s, 2H) ppm
4	p-PET, 200 min^{-1}	Terephthalic acid	**^{1}H-NMR** (d_6-DMSO, 400 MHz): δ = 8.07 (s, 4H), 13.32 (s, 2H) ppm
		Isophthalic acid	**^{1}H-NMR** (d_6-DMSO, 400 MHz): δ = 7.67 (t, J = 7.60 Hz, 1H), 8.19 (dd, J = 1.8, 7.76 Hz, 1H), 8.52 (t, J = 1.76 Hz, 1H), 13.32 (s, 2H) ppm

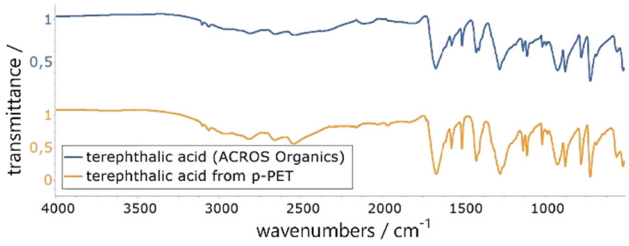

Figure 10: FT-IR-spectra of the obtained terephthalic acid in comparison with the terephthalic acid standard.

conditions and may be separated after PET depolymerization for further processing.

3.7 Classification of the results in the context of a concept for a PET-recycling process

Based on the presented results for the successful continuous depolymerization of bilayer p-PET waste, a process concept for a complete PET-recycling process may be derived. The high degree of depolymerization in the extruder within a few minutes thus provides a good starting point for the recovery of TA. The concept of recycling technology consists of seven process steps for the production of TA from waste PET material (see the process block diagram in Figure 12).

In the first step, depolymerization is conducted in a twin-screw extruder as a continuous reactor with an average residence time in the order of minutes. Twin-screw extruders are widespread machines in the plastic industry. Due to the modular design, extruders offer a wide range of options for especially adapting the thermal and mechanical conditions for processing the respective material.

In the next process step, disodium terephthalate in the extrudate is completely dissolved in water. The subsequent filtration and optional discoloration step, depending on the feed material, purify the solution from nonreacted and undesired compounds. In the following precipitation step, the TA is precipitated through the addition of a strong acid. The suspension is filtered, and the resulting TA is washed, recrystallized, and dried. EG can be recovered during the depolymerization process or following the purification of the filtrate.

With this process, it is possible to recover TA and EG from hardly recyclable PET waste and to close the raw material cycle. This innovative technological approach thus represents a promising possibility for the creation of a circular economy for PET waste. In future studies, this technological development should be complemented with economic and ecological investigations of the presented recycling technology.

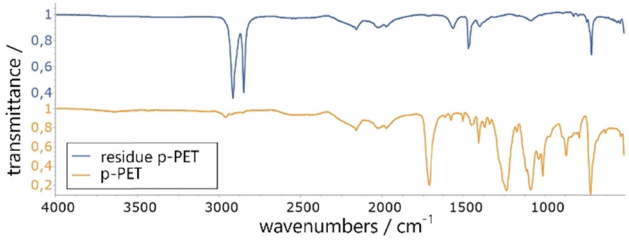

Figure 11: FT-IR-spectra of the residue of the depolymerized p-PET starting material.

4 Conclusions and outlook

The chemical recycling of PET via depolymerization in a twin-screw extruder was investigated with postconsumer PET bottles and bilayer PET/PE material as feedstocks. Within residence times in the order of minutes, disodium terephthalate and EG were obtained in yields of up to 97% for b-PET. High shear stress on the reaction mixture

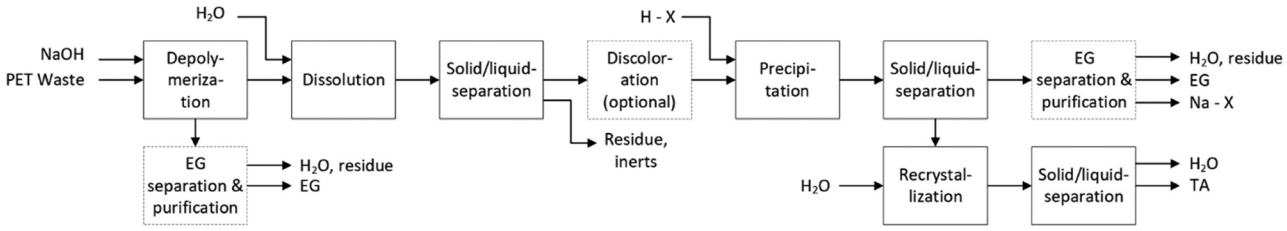

Figure 12: Block diagram of the continuous back-to-monomer recycling process.

allowed for short reaction times. The obtained monomer TA showed IR spectra highly similar to the standard commercial TA. For bilayer PET materials, the PE layers remained inert at depolymerization conditions in the extruder and may thus be separated subsequently for further processing.

Further studies should address the influence of process parameters, such as temperature, PET particle size, and stoichiometry, on the depolymerization of PET. Furthermore, the recovered TA should be polymerized, and the resulting polymer was characterized. Finally, further separation and purification of EG will be elaborated. Such experiments are planned for the future.

Considering the high volume of plastics worldwide (i.e., 250 million tons in 2018), the presented approach may serve as a useful recycling process for complex PET waste with high throughputs at low reaction times. In particular, the feasibility of reusing nonrecyclable fractions of postproduction and postconsumer waste opens up a novel avenue for the circular economy for PET materials. Moreover, this type of process intensification represents a novelty in the continuous depolymerization of PET.

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Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this article.

Data availability statement: The datasets generated during and analyzed during the current study are available from the corresponding author on reasonable request.

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